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Reviews

Supercritical Carbon Dioxide-Assisted Process In Synthesis of Polymer/Clay Melt

Norazlina Hashim*[,1] and Kamal Yusoh[2]

[1]*Faculty of Chemical Engineering Technology, TATI University College, 24000 Kemaman, Terengganu, Malaysia*
[2]*Faculty of Chemical and Natural Resources Engineering, University of Malaysia Pahang, 26300 Gambang, Pahang, Malaysia*

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Abstract: Nanocomposites are currently being used in a number of fields, and new applications are continuously being developed including mechanical and biomaterial devices, as well as various in solar and fuel cells applications. Generally, the synthesis of polymer nanocomposites are done using solution chemistry, and this may raise serious concerns regarding air and water pollutions. Immediately, the 'green' method using supercritical carbon dioxide ($scCO_2$) has grabbed the attention of researchers who are responsible to synthesize polymer composites by non-hazardous routes. Extrusion processes would benefit from the use of $scCO_2$ since the rationale of the extrusion process is to formulate, provide texture and shape molten polymers by forcing them through a die. $ScCO_2$ has been used in several studies as a medium of clay dispersion in polymer matrix by providing a solvent-free fabrication route for nanocomposites. Furthermore, it has more favorable interactions with polymers compared to other inert gases and has the ability to be dissolve in large quantities. It acts as a plasticizer, which modifies viscosity and interfacial properties of the polymer drastically. In this paper, experimental and theoretical studies of solubility and viscosity of several polymer melts in clay are discussed in detail. The assistance of $scCO_2$ in clay dispersion and as a foaming agent has been reviewed extensively.

Keywords: supercritical carbon dioxide, melt processing, clay nanocomposites, nanofiller dispersion, foaming.

Introduction

Supercritical fluids have been well known as alternative foaming agents in various polymers and nanocomposite systems. Recently, supercritical carbon dioxide ($scCO_2$) has also been used in much research as a medium of filler dispersion in polymer matrix by providing a solvent-free fabrication route for nanocomposites. A standout reason for using nanofillers in polymer composites compared to the micron-sized particles is the large surface area or interaction zone that nanofillers provide per unit volume of particle used. Due to this reason, nanofillers cater superior physical and mechanical properties. Unfortunately, most commercial nanofillers tend to agglomerate due to drying process during synthesizing. To achieve the superiority of nanofillers mentioned earlier, the agglomerates must be broken to assist the dispersion of individual nanofillers. The dispersion of nanofiller agglomerates can be achieved by melt, solution and *in situ* processing. Both solution and *in situ* methods have achieved more success in dispersion approach, but due to the intrinsic disadvantages such as chemical hazards and limitations in a batch process, the methods are of minimal interest. From the industrial point of view, melt processing or mechanical compounding is the preferable method because of the short processing time, the absence of solvents and the compatibility with industrial manufacturing techniques. However, in the absence of compatibilizers, the process has limited success. Melt and solution processing primarily result in intercalated nanocomposites, and *in situ* polymerization provides a range of dispersion from intercalated and exfoliated nanocomposites.[1,2] Although processing with supercritical fluids has been used since the early 1990s,[3,4] only polymer-clay composites have monopoly the attention of researchers.

The objective of this paper is to investigate the effects of $scCO_2$ on nanoclays dispersion in nanocomposites using various polymers.

Supercritical Carbon Dioxide ($scCO_2$)

A supercritical fluid (SCF) is any substance at a temperature and pressure above its thermodynamic critical point that provides a novel route to the dispersion of nanofiller agglomerate. It

*Corresponding Author. E-mail: norazlinatatiuc@gmail.com

has unique features such as liquid-like density and gas-like diffusivity, which are important for dissolving many compounds and implication for reaction kinetics.[5] An SCF system must have either a high degree of miscibility with the polymer matrix of the nanofillers, or with the organic modifier of the nanofillers. During rapid depressurization, the SCF changes to the gas phase, and furthermore, it tends to separate and disperse agglomerates. Understanding the phase behaviour of the polymer/SCF/nanofiller system can explain how rapid gas expansion caused the dispersion of nanofiller in polymer matrix.

As a substitute for organic solvent, the SCF must be compromised by many factors such as the cost of high-pressure reactors and continuity. Solvents with low critical constants will reduce this cost due to easy handling, solvent reactivity and safety factors. Most of the organic solvents suitable for supercritical applications such as ethane are flammable and can be harmful. Another suitable solvent, water, is non-toxic but the high parameters (critical temperature, T_c=374.4 ºC and critical pressure, P_c=22.12 MPa), as well as corrosion problems with metal reactors, limit its wider application.

Due to its moderate critical constants (T_c=31.0 ºC, P_c=7.38 MPa) (Figure 1), non-flammable and harmless, carbon dioxide (CO_2) is the most commonly used solvent as an SCF. CO_2 is not only readily available abundantly, but it can also be produced as a by-product in ammonia, hydrogen and ethanol plants, as well as in electrical power generation stations.[5] Besides reducing the viscosity of molten polymer due to an increase in free volume, dissolved CO_2 can also alter physical properties of polymers including density, diffusivity and swollen volume. Therefore, it has a great opportunity to be used a plasticizer at high temperature in polymer processing.[6]

In many years, $scCO_2$ has been used in polymer modification, polymer composites, microcellular foaming, particle production, polymer blending and polymerization. Chemical modification of polymers can be performed in milder conditions compared to standard methods of melt modification in extruders or batch mixers. This method is suitable for polymers with critical temperature consideration such as poly(tetrafluoroethylene) (PTFE)[7] and polypropylene (PP),[8-10] in which modification in the melt is normally accompanied by degradation. Most research used chemical grafting (by radical mechanisms) of monomers onto PP to modify its hydrophilicity. Several studies have reported to successfully grafted monomer onto PP in CO_2-assisted processes such as methyl acrylate,[11] methyl methacrylate,[12-14] styrene[13,15] and maleic anhydride.[16,17] The presence of CO_2 does not modify the mechanism of radical grafting but it provides better dispersion of the reactive species in the PP matrix at low processing temperature. Polymer composites consisting of inorganic or organic materials incorporated into polymeric matrix have received serious attention by researchers due to their growing applications in electronic, optical, medical and mechanical devices. A few systems have been reported involving micro- and nano-sized particles.[18-24] In several cases, supercritical CO_2 acts not only as a plasticizer for the synthesized polymer matrix, but also as a carrier facilitating the absorption of monomer into fibers or particles.

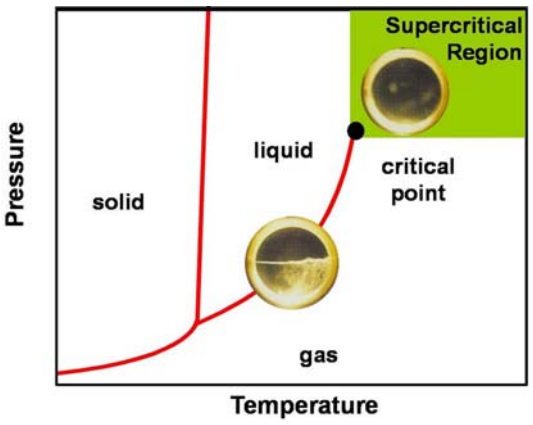

Figure 1. Carbon dioxide pressure-temperature phase diagram.

The implementation of $scCO_2$ in microcellular foaming provides many advantages, including narrow cell size distribution, easy solvent recovery, good plasticizing ability and high diffusivity. The replacement of various hazardous traditional blowing agents such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and volatile organic compounds (VOCs)[25-27] is a good indication that SCF can be used as an option to assist in processing. Traditional method dissolves the blowing agent in polymer matrix. The solubility of the blowing agent is reduced rapidly by increasing temperature or decreasing pressure to produce thermodynamic instability in the structure, which will induce nucleation and growth of bubbles. In foaming process, the fabrication involves both solid state and melt foaming processes. The prerequisite of the process is high amorphous fraction of material tested. Crystalline polymers such as poly(lactic-*co*-glycolic acid) (PLGA) and semicrystalline poly(lactic) acid (PLA) do not form proper porous structures. The existed crystalline regions not only depress the solubility of CO_2 in the polymer matrix, but also affect cell nucleation and bubble growth tremendously.[28-32] The melt process for fabricating PLA foams such as foam extrusion[33,34] and batch foaming[35] processes can avoid the drawbacks raised by the crystal regions. However, as in other polyester, the linear molecular chain structure of PLA does not confer much elasticity at melt state.[36] This is unfit in the foaming process since melt strength is required to stabilize the foam structure prior to cooling and foam solidification. Another drawback of using current melt process is the slow crystallization kinetics behaviour of PLA that obtained low crystallinity PLA foams and can affect the mechanical properties of polymer products.[37] All of these problems can be overcome by using $scCO_2$. Two types of microcellular foaming, batch foaming and continuous microcellular foaming, can be implemented in foaming nanocomposites. Several research

groups have reported batch foaming of various polymers.[38-40] A polymer in disc or powder is subjected to $scCO_2$ without mixing. Dissolved CO_2 decreases the glass transition temperature or melting point to convert the polymer to a molten state. A drawback of batch process is relatively low diffusivity of gas, which results in long cycle times. This problem can be solved in continuous microcellular foaming by providing rapid mixing of polymer and CO_2. Extrusion technique is generally used for mixing polymer and gas. In an extruder, the single-phase solution formation time decreases as high shear mixing decreases the gas diffusion distance.[6,41]

Particle formation method using $scCO_2$ as a solvent and antisolvent gives benefits such as better control of particle size, morphology and particle size distribution. Several methods have been broadly reviewed[42-51] and implemented, including rapid expansion of supercritical solutions (RESS),[52-64] solution-enhanced dispersion by supercritical fluid (SEDS),[65-77] gas antisolvent crystallization (GAS),[78-85] supercritical antisolvent precipitation (SAS),[52,77,86-88] precipitation by compressed antisolvent (PCA),[89-94] aerosol solvent extraction system (ASES)[95-102] and particle from gas-saturated solutions (PGSS).[52,103-107] These methods are widely used in biodegradation polymers that are implemented in biomedical devices. Another application of $scCO_2$ is in polymer blending. Polymer blending is the process in which two or more immiscible polymers are mixed with each other in non-reactive or reactive ways. In the non-reactive route, two immiscible polymers are blend in the molten state and form two phases. Generally, high-power batch mixers and twin screw extruders are mostly used in the process employing CO_2 as a plasticizing agent. CO_2 reduces the viscosity of the component to allow better dispersion. On the other hand, in the reactive route, $scCO_2$ assists the infusion of reagents (monomer and initiator) into polymer and the subsequent polymerization reaction within the host polymer. For efficient blending, the monomers and initiator must be soluble in $scCO_2$, and the solubility of CO_2 in the host polymer is high enough to cause it to swell. Free radical dispersion polymerizations in $scCO_2$ have been extensively studied since the 'green' properties of SCF have been recognized.[108-115] $ScCO_2$-assisted process decreases the viscosity of polymerization and reduces mass transfer resistance. As viscosity depends on the amount of CO_2 dissolved, the solubility of CO_2 in the synthesized polymer carries a crucial role in determining the ultimate molecular weight and properties of the polymer.

In synthesizing nanocomposites, Manke *et al*.[116,117] patented two methods to produce PP/clay nanocomposites with the assistance of $scCO_2$. A similar procedure was applied in extrusion foaming to produce clay nanocomposites of high-density polyethylene (HDPE) and poly(trimethyleneterephthalate) (PTT) using $scCO_2$, which increased to 33% in typical clay d-spacing for HDPE/clay nanocomposites, while an increase of 10% was observed for PTT/clay nanocomposites.[118] Tomasko *et al*.[119] wrote an extensive review on various applications of $scCO_2$ for polymer synthesis and processing. In 2006, a wider application of $scCO_2$ has been discussed by Nalawade *et al*.[6] Recently, Haldorai *et al*.[5] covers a review on synthesis methods of polymer-inorganic filler nanocomposites in $scCO_2$.

SCF-Assisted Processes in Dispersion of Clay in Polymer Matrix

The simplest method of preparing polymer/nanofiller nanocomposites is direct mixing of the nanofiller into the polymer. The mixing can be done by melt and solution blending. The main problem encountered in the mixing process is the effective dispersion of nanofillers in polymer because nanofillers tend to agglomerate. A few weight percent of layered silicates dispersed in polymer matrix can create higher polymer/nanofiller interaction. Three types of polymer/layer silicate (PLS) nanocomposites can be classified depending on the strength of nanofiller interactions; intercalated, flocculated and exfoliated nanocomposites (Figure 2).[120] In intercalated nanocomposites, the silicates are arranged well and orderly by interlayers within polymer, and the properties are likely as ceramic materials. The concept of flocculated nanocomposites is similar to intercalated nanocomposites, but at some times, silicate layers are flocculated due to hydroxylated edge-edge interaction. In exfoliated nanocomposites, individual clay layers are separated and homogenously dispersed in polymer matrix as the interlayer forces are completely destroyed to allow free movement of silicate layers away from each other.[8,9]

Melt intercalation method becomes a primary choice in the preparation of polymer/layer silicates (PLS) nanocomposites. The degree of delamination of silicate platelets and dispersion

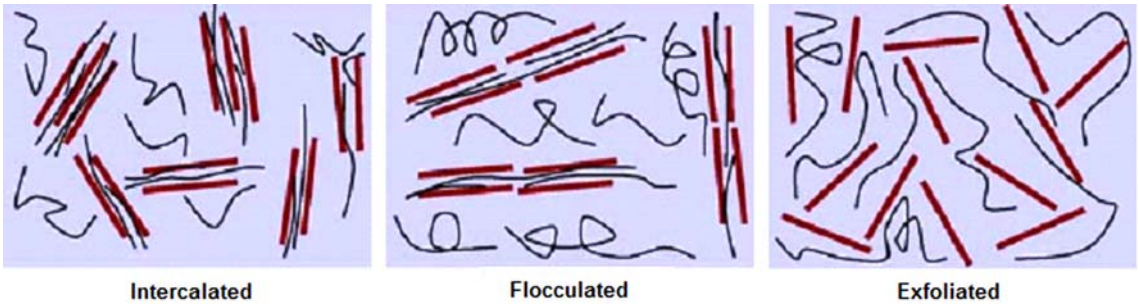

Figure 2. Three types of polymer/layer silicates nanocomposites.[120]

in polymer matrix are dependent on the melt intercalation process. Co-rotating patterns of twin-screw extruder would be the first choice in synthesizing PLS nanocomposites due to shear and intense mixing.[5,11] The ability of silicate particles to disperse into individual layers and the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations are two factors that must be considered during mixing to enhance dispersion.[121] The melt intercalation route is usually achieved by twin-screw extrusion, and the process conditions that should be considered are the feed rate, screw speed, operating temperature, and also mixing sequences, such as direct mixing or dilution of masterbatches. These factors influence the dispersion quality of blending significantly.

The capability of $scCO_2$ to reduce melt viscosity and to delaminate silicate layers is demonstrated by increasing inter-chain distance and free volume, thereafter reducing inter-chain interactions. Ma *et al.*[122] successfully prepared well-dispersed polypropylene (PP)/sepiolite clay nanocomposites using $scCO_2$-assisted mixing with and without the presence of maleic anhydride grafted PP (PP-*g*-MA) as a compatibilizer. A comparison was made with the work by Bilotti *et al.*,[123] where the PP/sepiolite nanocomposites were prepared by using traditional melt compounding. Figure 3 shows the scanning electron microscopy (SEM) images of nanocomposites from both studies. The large aggregates of sepiolite fibres observed in melt compounded PP/sepiolite (circled regions in Figure 3(a) and (b)) are not observed in the $scCO_2$ PP/sepiolite nanocomposites, which confirms better dispersion of clay in $scCO_2$. The images from transmission electron microscopy (TEM) indicate sepiolite needles are separated from each other in $scCO_2$ PP/sepiolite nanocomposites and the fibre length of about 400-500 nm could still be preserved, which is much longer than those of

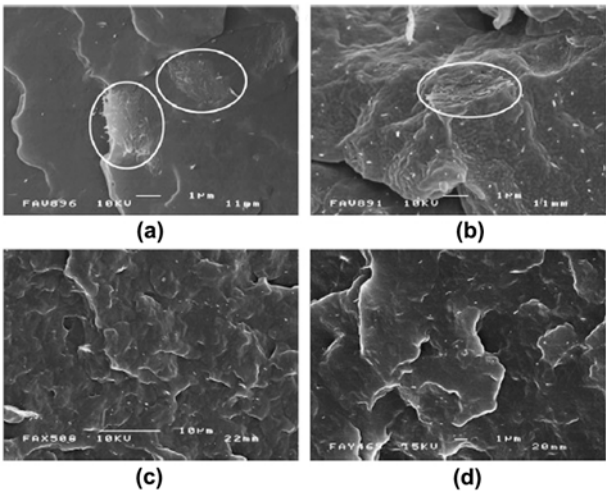

Figure 3. SEM images of samples for (a) melt-compounded PP/sepiolite (2.5 wt%);[123] (b) melt-compounded PP/PP-*g*-MA (2.5 wt%)/sepiolite (2.5 wt%);[123] (c) $scCO_2$ PP/sepiolite (2.5 wt%);[122] (d) $scCO_2$ PP/PP-*g*-MA (2.5 wt%)/sepiolite (2.5 wt%).[122]

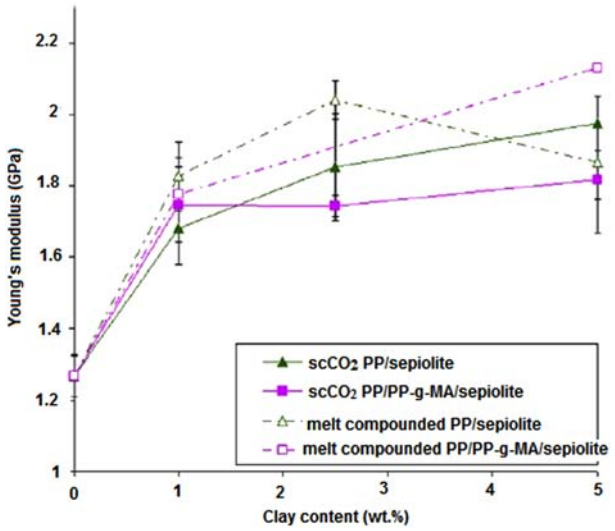

Figure 4. Young's modulus of PP/sepiolite nanocomposites at different clay contents prepared by melt-compounded and $scCO_2$ methods.[122]

sepiolite fibres in the melt compounded samples. This notifies that $scCO_2$ can prevent breakage and aggregation of sepiolite and lead to higher reinforcing efficiency.

The results of mechanical properties showed no significant effect of using a compatibilizer, PP-*g*-MA, in melt compounding compared to the process using $scCO_2$ and without the presence of a compatibilizer. For melt-compounded samples, the Young's modulus showed 9% reduction for clay content of 2.5 to 5 wt% (without compatibilizer), whereas for compatibilizer-added samples, 68% increase in modulus was shown for clay content of 1 to 5 wt% (Figure 4). For the samples prepared using $scCO_2$ processing, the plot with compatibilizer remains

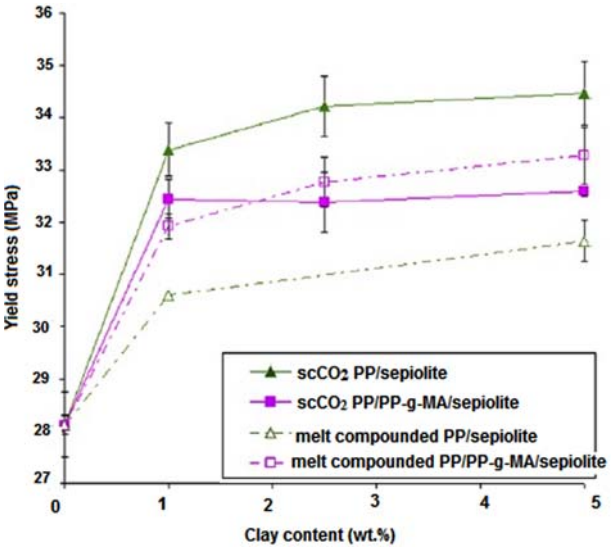

Figure 5. Yield stress of PP/sepiolite nanocomposites at different clay contents prepared by melt-compounded and $scCO_2$ methods.[122]

roughly constant across the differing clay contents. The plot without compatibilizer showed a steady increase in modulus especially for 5 wt% sepiolite, which gives 56% increment. Figure 5 shows an increase in yield stress for $scCO_2$ PP/sepiolite nanocomposites up to 23% for 5 wt% sepiolite samples compared to pure PP, and a clear increase over those prepared by melt compounding. Moreover, $scCO_2$ PP/sepiolite nanocomposites without compatibilizer possess higher yield stress than those with compatibilizer. This confirms the good dispersion of sepiolite in PP matrix and the function of fibre length in the $scCO_2$-assisted process. All these facts proved that the PP/sepiolite nanocomposites prepared in $scCO_2$ have improved significantly, especially in the absence of PP-*g*-MA.

In order to improve clay dispersion *via* melt blending methods, some authors reported on the use of masterbatch techniques.[14-16] This method consists of polymer/clay blends with high weight percentage of clay prepared by melt blending. Then, the blends are redispersed (diluted) into polymer matrix, but this technique usually leads to semi-intercalated/semi-exfoliated morphology.[124] An impressive masterbatch production has been previously described by Dubois *et al.*[125] using poly(ε-caprolactone) (PCL) and poly(vinyl chloride) (PVC). A highly filled polymer/organo-modified silicate clay nanocomposite was synthesized by *in situ* intercalative polymerization of monomer in the presence of high amount of clay (25-50 wt%) and catalyzed by dibutyltin dimethoxide. The final nanocomposite was obtained by melt blending with a different amount of well-dispersed clay (1-10 wt%). This research yields intercalated/exfoliated morphology nanocomposites with efficient dispersion of clay platelets and shows higher stiffness for PCL nanocomposites even with non-modified natural clay, *i.e.*, sodium montmorillonite (MMT-Na^+), which could not be obtained by direct melt blending. Instead of these interesting results, this process has faced the complexity to recover aggregated bulk masterbatch and there is a necessity to purify masterbatch before use. After a few years, Dubois *et al.*[126] came with another research that synthesized chlorinated polyethylene (CPE)/PCL/clay also using masterbatch approach. Initially, a high clay content of masterbatch-based on PCL (as a compatibilizer) was produced and then dispersed by melt blending with CPE. The low molecular mass of PCL (M_n=4,000 g mol^{-1}) gave rather intercalated structure but their ultimate properties remain unchanged. Besides that, with higher molecular mass of PCL (M_n=50,000 g mol^{-1}), clay delamination is favoured, hence leads to improvement of thermal and mechanical properties. However, from the TEM results and supported by wide-angle X-ray diffraction (WAXD) analysis, the silicate was not completely exfoliated into randomly distributed individual sheets within CPE matrix. Urbanczyk *et al.*[124] prepared PCL nanocomposites masterbatches by *in situ* intercalative polymerization in $scCO_2$ using stannous octoate $Sn(oct)_2$ as a catalyst with highly filled-clay (33-66 wt%). An easily recoverable fine powder was synthesized after depressurization, and its capacity to extract residual monomer during depressurization are among the benefits of using $scCO_2$ process compared to conventional direct melt blending. The PCL/clay masterbatches were then redispersed in CPE that is miscible to PCL. Upon dispersion of the masterbatches in CPE, the clay was largely delaminated compared to direct melt blending of commercial clay. $Sn(oct)_2$ had been chosen as the polymerization catalyst due to its lower sensitivity to protic impurities and has less sensitivity to carbonation reaction on the catalyst, which this phenomenon can decrease polymerization rate. Another work by Urbanczyk *et al.*[127] using the same approach was reported by synthesizing polylactic acid (PLA)/clay nanocomposites. The *in situ* polymerization of monomer, D,L-lactide and high clay percentage (35 wt% and 50 wt%) catalyzed by tin(II) octoate was perform using $scCO_2$ process. The materbatches were dispersed into L-PLA by melt mixing using twin-screw extruder. The aim of the monomer is to introduce an amorphous phase in the semi-crystalline L-PLA for grafting to the nanoclay, hence homogenously distributed in matrix to enhance material impact resistance. Intercalated or exfoliated nanocomposites were produced depending on the functional group borne by the organo-clay at low clay level (3 wt%). TEM and XRD analyses confirmed good exfoliation degree, and these well-delaminated PLA/clay (3 wt%) nanocomposites showed significant improvement in both stiffness and toughness compared to the unfilled PLA.

SCF as Foaming Agents in Nanocomposites

Polymer/clay nanocomposites foams are suitable for many industrial applications such as airplane and automotive parts, thermal insulation and microelectronic applications. These applications can be widely expanded when microcellular materials are obtained where the porosity has cell density higher than 10^9 cells cm^{-3} and cell size lower than 10 μm.[21,22] Actually, foaming of semicrystalline polymers is harder compared to the foaming of amorphous polymers. Since gas only diffuses through amorphous regions, it does not dissolve into crystallites below the mixture's melting point; hence, hinders gas diffusivity through the polymer matrix.[128] To overcome this problem, the polymer saturation process must be done at higher temperature than the melting point of a polymer-$scCO_2$ system.[22-24] After the saturation at high temperature, the system is rapidly cooled and immediately, depressurization takes place, resulting in supersaturation and lastly, gas nuclei/pores are developed inside the polymer matrix. Otherwise, the saturation can proceed at lower temperature but with the addition of co-solvents, which enhance the melting point depression of the polymer-SCF system and subsequently enhances the solubility of the SCF in the polymer matrix.

The ability of nanoparticles to disperse in polymer matrix during $scCO_2$ processing has an effect on foam structure. Improved dispersion of clays and modified porous structures have been obtained with $scCO_2$, mainly in a batch process *via* the *in situ* intercalation method involving several

nanocomposite systems such as polystyrene (PS)/clays,[129] polydimethylsiloxane (PDMS)/clays,[130] and polylactic acid (PLA)/clays.[131] Continuous processes such as $scCO_2$-assisted extrusion or injection are easily adaptable for an industrial scale-up. Plasticization capacity decreases the viscosity of molten polymer during processing and limits the mechanical stresses and operating temperature.[132] This is particularly important for polymers having limited thermal stability such as biopolyester. A growing number of studies have been reported on the preparation of nanocomposite systems with clays nanofiller using $scCO_2$-assisted approach in continuous processing. Several methods that have been used include two-step extrusion process,[133-135] single-screw extrusion,[136] single-screw extrusion with prior preparation of exfoliated nanocomposites by *in situ* polymerization[137] and injection of $scCO_2$/clays mixtures in extruder.[138,139] In most cases, the researchers obtained positive findings, where cell density increased with smaller cell size and the performances of exfoliated nanocomposites foams have been improved.

Well-dispersed foam of poly(methyl methacrylate) (PMMA)/modified silica nanocomposites were prepared by Goren *et al*.[140] The surface of silica nanoparticles were modified with fluorine containing silane coupling agent, tridecafluoro-1,1,2,2-tetrahydrooctyl silane (TFTOS), to prevent agglomeration. The modified silica was premixed with PMMA and then fed to a Haake MiniLab twin-screw extruder at 200 °C. Then, the polymer nanocomposites were placed in an autoclave and soaked with CO_2 at different pressures; 6.9, 9.7, 12.4, 15.2, and 17.9 MPa. Radial distribution functions (RDF), G(r) were constructed to characterize the dispersion and distribution state of nanoparticles and calculated with a bin size of 250 nm (Figure 6). In the non-CO_2 (0 MPa) processed sample, the peak in the first bin represents agglomeration of primary particles as there was poor interaction between the fluorinated surface modifiers and PMMA. After CO_2 processing, the first peak (indicating agglomeration) showed a drastic drop in intensity, whereas secondary peaks indicated better dispersion and distribution of primary particles. From the finding, it can be concluded that saturation of PMMA/silica nanocomposites with $scCO_2$ improves dispersion of nanoparticles, which then increases saturation pressure and results in better dispersion of silica in matrix. Furthermore, surface modification of silica decreases the surface free energy for CO_2 nucleation, which consequently increases the probability of dispersed nanoparticles.

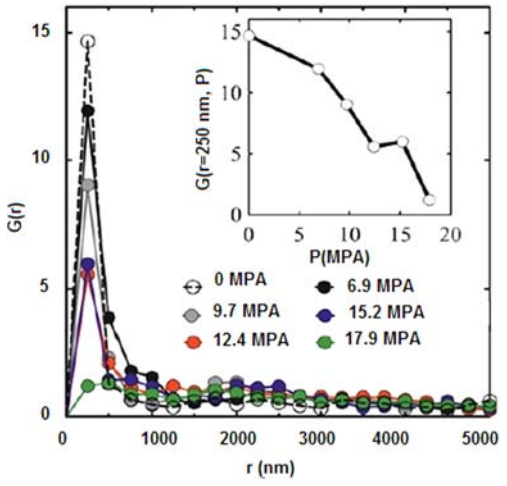

Figure 6. Primary particle radial distribution functions (RDFs) at various CO_2 saturation pressures. The inset shows the value of RDFs for the first peak as a function of saturation pressure.[140]

The two-step extrusion process in nanocomposites foams involves two stages of processing. In the first step, the nanocomposite matrix is prepared by solution casting or extrusion techniques.[120] In the second step, the porous structure is obtained *via* supersaturation by exposing the nanocomposites to SCF atmosphere.[25,26] Besides CO_2, several researchers have used ethanol or a mixture of CO_2/ethanol as supercritical fluids to assist the process, thereafter enhances the dispersion of nanofiller in matrix. In this part, several researches are discussed using mixtures of SCF fluids for polymer and polymer/clay nanocomposites. Tsimpliaraki *et al*.[141] studied the effect of properties of PCL/clay nanocomposites prepared by one-step process and two-step process using CO_2 and ethanol

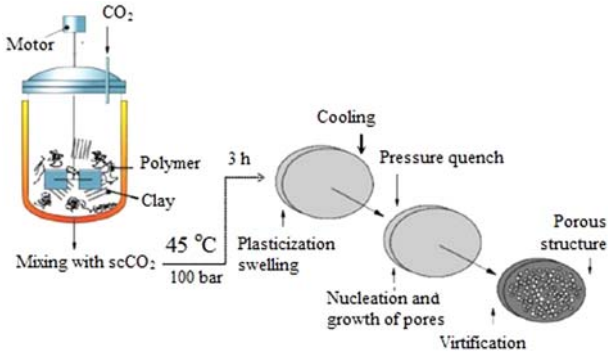

Figure 7. One-step process: Clay dispersion and foaming with the aid of $scCO_2$-ethanol mixtures ($\chi_{ethanol}$=0, 0.015, 0.030, 0.059, 0.088).[141]

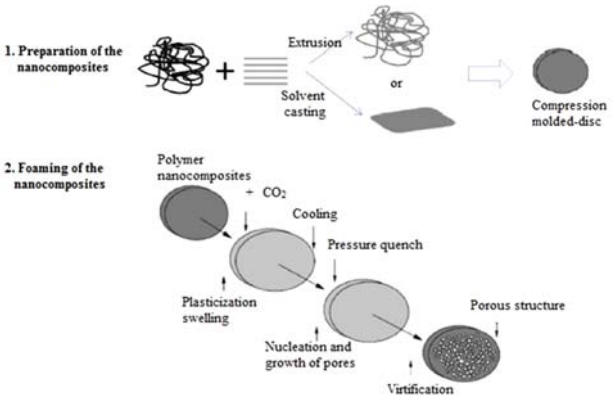

Figure 8. Two-step process: Preparation of nanocomposites *via* (1) conventional approach and (2) foaming with the aid of $scCO_2$ (CO_2-ethanol, $\chi_{ethanol}$=0.030).[141]

as fluids, whereas the clay content was kept constant at 5 wt% (Figure 7 and Figure 8).

From X-ray diffraction (XRD) analysis, all samples prepared with CO_2-ethanol mixtures presented lower 2θ values from the pristine clay, indicating a successful intercalation of PCL into the clay with even such low amount of ethanol (ethanol fraction, $\chi_{ethanol}$=0.015), which is sufficient for clay intercalation. A one-step method is possible to obtain similar results in terms of clay dispersion in the polymer produced using two-step method ($\chi_{ethanol}$=0.030), which support that SCF systems can be an alternative method for the preparation of nanocomposites. SEM images (Figure 10) also showed no difference on nanocomposite structures between one-step and two-step methods (solvent casting and melt blending) using ethanol fraction of 0.030. Despite these results, the addition of ethanol in CO_2 mixtures changed the morphology of nanocomposite structures in the one-step process as shown in Figure 9. Poor clay dispersion and non-uniform porous structure were obtained when pure CO_2 was used as a dispersion medium. Contrary to the samples that were prepared with pure CO_2 as a blowing agent, more uniform cell structures were obtained using CO_2-ethanol mixtures, and it is applicable when high porosity is needed. These results are in agreement with other researches.[27,28] Additionally, Tsivintzelis *et al.*[142] studied the

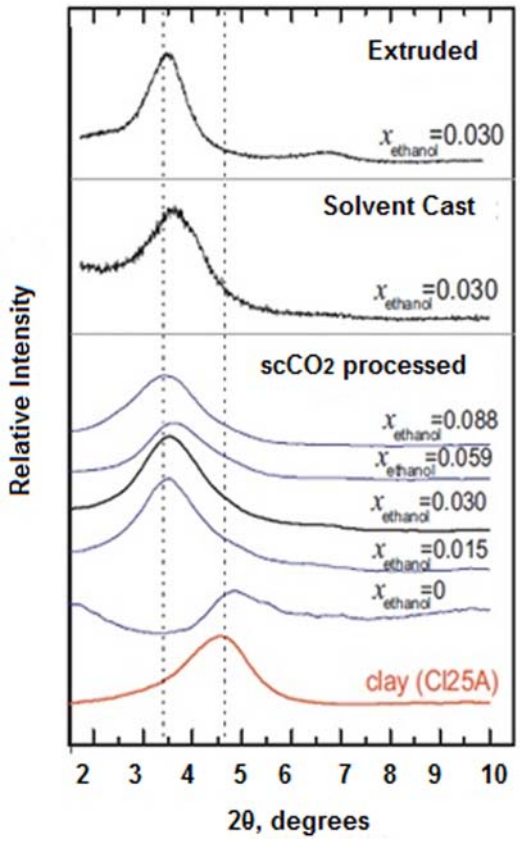

Figure 9. XRD patterns of clay and PCL/clay nanocomposites prepared *via* $scCO_2$, solution and melt blending.[141]

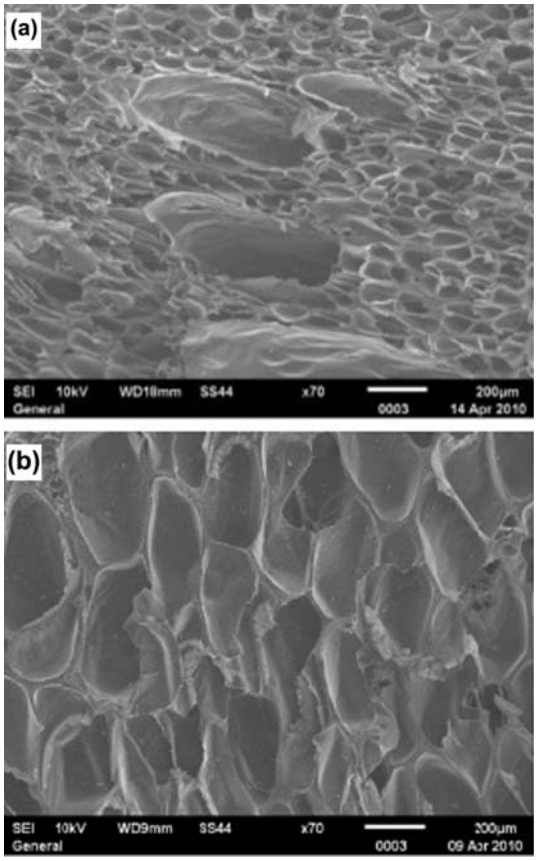

Figure 10. Porous PCL/clay structures using (a) pure CO_2, $\chi_{ethanol}$ =0 and (b) CO_2-ethanol mixtures, $\chi_{ethanol}$=0.030.[141]

effect of temperature and pressure on the final porous structure of PCL. At constant temperature of 35 °C, they conducted the study using CO_2-ethanol ($\chi_{ethanol}$=0.008), while the pressure ranged between 123 and 205 bar. The increase of pressure enhanced CO_2 solubility in the polymer matrix, as predicted by the nucleation theory, the energy barrier to nucleation decreases.[142] During the depressurization time, more nuclei were formed, resulting in the production of more cells with smaller size. At larger pressure, more fluid dissolved into the polymer matrix available for nucleation and growth of pores, which also increased the nuclei formed that share this fluid. It is observed in Figure 11 that bulk foam density decreases as pressure increases. The effect of temperature was studied between 35 and 45.1 °C at constant pressure of 147 bar with the same mol fraction of ethanol as before. The results showed that a small increase of temperature did not lead to a significant effect in the average pore size (Figure 12), but decreased the bulk foam and cell density slightly.

Kiran[144] reported the foaming of bioabsorbable copolymer, poly(ε-caprolactone-*co*-lactide) (PCL-LA) in CO_2 and CO_2-acetone mixtures. The work was conducted in a specially designed mold with porous metal surfaces at 60, 70, and 80 °C and 7-28 MPa ranges of pressure. The foams with pores in

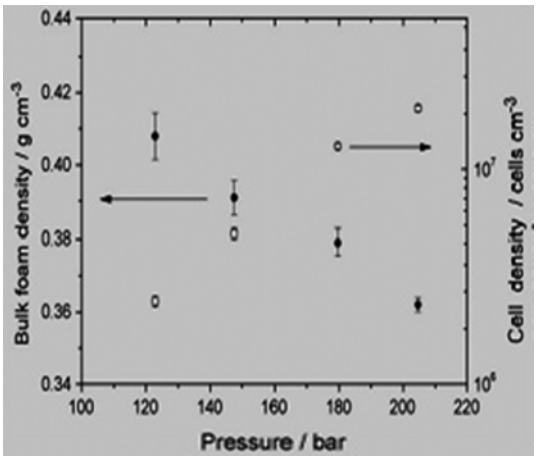

Figure 11. Cell and bulk foam density as a function of pressure.[142]

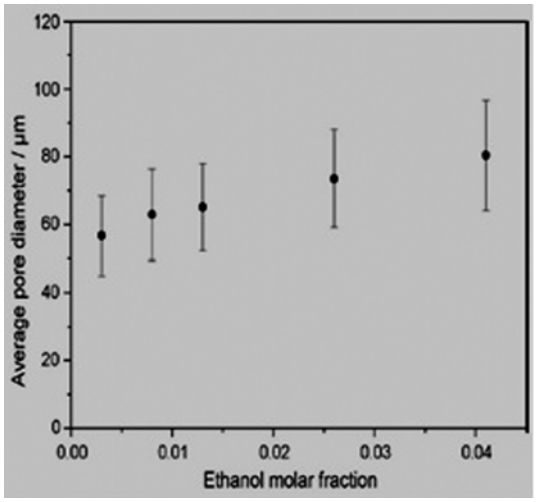

Figure 12. Average pore diameter at constant pressure.[142]

the range of 5 to 200 μm were generated depending upon the conditions. The foams pores uniformity of copolymer obtained in CO_2-acetone had improved compared to foams formed in pure CO_2. This research was also extended by forming porous tubular constructs by PMMA extrusion solutions composed of either mixtures of 50 wt% polymer and 50 wt% acetone, or 25 wt% polymer, 10 wt% acetone and 65 wt% CO_2 at 70 ºC and 28 MPa. Long, uniform porous tubular with 6 mm ID and 1 mm wall thickness with pore sizes in the range 50 μm range were generated. Tubular foams of the copolymer with interconnected pores in the sizes around 50 μm were also generated by extrusion solution composed of mixtures of 25 wt% polymer, 10 wt% acetone and 65 wt% CO_2 at 70 ºC and 28 MPa. Reducing the acetone content in the solution led to the reduction of pore sizes, which was proven by environmental electron microscope (ESEM) analysis.

Recently, the effect of nanoclay on the foamability of biodegradable polymer produced from renewable agriculture materials of PLA has been investigated.[145,146] Keshtkar *et al*. studied the effect of clay content (0-5 wt%) in continuous extrusion PLA nanocomposites foam blown with $scCO_2$.[146] The XRD and TEM analyses showed a high degree of exfoliation of clay nanoparticles (Cloisite 30B) within PLA. A single-screw tandem extruder was used to produce foams with 5 wt% and 9 wt% $scCO_2$. They reported that in the presence of dissolved CO_2, clay and shear action, the kinetics of PLA crystallization enhanced significantly. Both the cell density and expansion ratio were greatly promoted with increased clay content and dissolved CO_2 (Figure 13). By further using Cloisite 20A nanoparticles with poor disperse ability in PLA, they also obtained a high degree of dispersion, which promoted the cell density and expansion ratio of the PLA nanocomposites significantly. In earlier year, Fujimoto *et al.*[147] also investigated the effect of nanoparticle dispersion on the foaming properties of PLA nanocomposites using a batch foaming system. They observed that the cell density increased dramatically with a better dispersion of the intercalated silicate, which was similar to the findings by Keshtkar and co-workers.

Besides PLA, many researchers studied on bio-based poly-

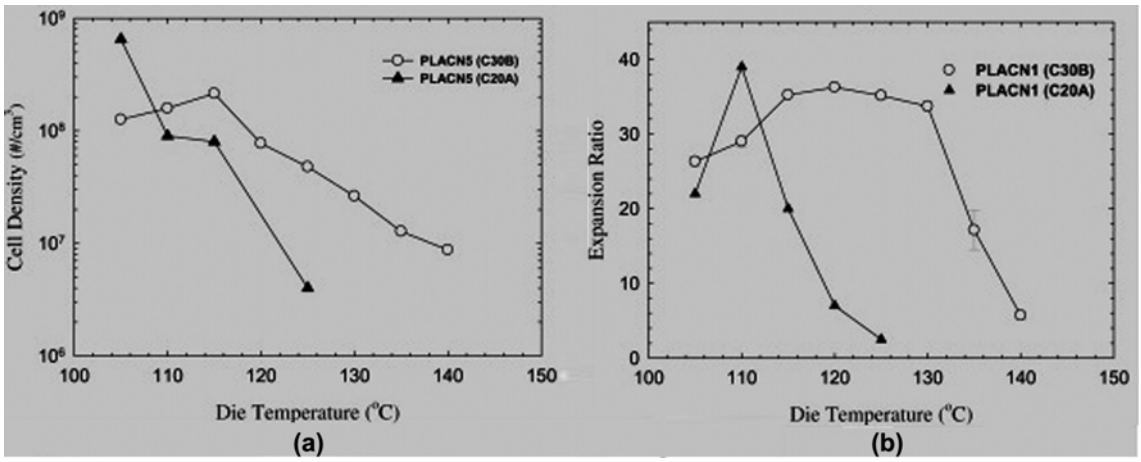

Figure 13. Comparison of (a) cell density and (b) expansion ratio of PLACN1 (PLA/1 wt% clay) prepared using Cloisite 20A (C20A) and Cloisite 30B (C30B) at various extruder die temperatures.[146]

mers, such as polyhydroxyalkanoates (PHAs), a member of polyester group, as eco-friendly alternatives to the current non-biodegradable polymers. Poly-3-hydroxybutyrate (PHB) is one of the PHAs members and has been most widely studied. However, the effectiveness of this alternative to oil-based thermoplastics is restricted by its high brittleness, slow crystallization rate and poor thermal stability, which makes it difficult to process.[148-150] As a substitution, several types of PHAs copolymers have been studied in previous research, such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) with various hydroxyvalerate (HV) contents and molecular weights, which present better mechanical properties, lower melting point and an extended processing window.[132,151]

Moigne *et al*.[132] prepared PHBV/organo-clays nanocomposite foams by two methods; a one-step method based on the direct foaming of physical PHBV/clays mixtures, as well as a two-step method based on the foaming of extruded PHBV/clays mixtures prepared beforehand by twin-screw extrusion. It has been proven that the prior preparation of a masterbatch by twin-screw extrusion and its dilution during the foaming process is a necessary step to improve clay dispersion without extensive thermal degradation of PHBV. Good clay dispersion appears by controlling the $scCO_2$ mass fraction in a narrow window to favour homogeneous nucleation while limiting the coalescence of pores. Furthermore, this allowed nano-biocomposite foams to be obtained with better homogeneity and higher porosity up to 50%. Instead of using $scCO_2$, Zhao *et al*.[152,153] investigated the possibility to use supercritical nitrogen (scN_2)-assisted injection molding process to develop microcellular PLA/PHBV/clays nanocomposites. The analysis showed a decrease of the average cell size and an increased cell density with the addition of clays in PLA/PHBV blends. Rheological behaviour of the PLA/PHBV/clays nanocomposites suggests a good dispersion of the clay within the matrix. PLA/PHBV/clays nanocomposites also possess higher modulus and greater melt strength than PLA/PHBV blends. As a crystalline nucleating agent, nanoclay enhanced the crystallinity of PHBV in the blend tremendously, thus leading to relatively high modulus for both solid and microcellular specimens. However, the addition of nanoclay in the blends had less effect on the tensile strength and strain-at-break. Javadi *et al*.[154] studied on PHBV-poly(butylene adipate *co*-terephthalate) (PBAT)-hyperbranched-polymer (HBP)-nanoclay (NC) assisted scN_2. Nanoclays exhibited intercalated structures in solid components but showed a mixture of exfoliated and intercalated structures in the microcellular nanocomposites. The addition of HBP and NC reduced the cell size, increased the cell density and enhanced the degree of crystallinity of microcellular components. Moreover, with the addition of HBP, the area under tan curve, specific fracture toughness and strain-at-break of the PHBV-based nanocomposite increased significantly. Table I shows several studies of PLA/clay blends using supercritical fluid.

SCFs as an Optional Technology in Industries

Liquid energy from renewable biomass is widely regarded as one of the greener alternatives due to the concerns of climate change and environmental pollutions that produced from fossil fuels. Current research and technology has been focusing on transforming these bio-resources into efficient liquid and gaseous fuels, and at the same time, they can produce multi-component products which can be further upgraded into higher value products. Unfortunately, in biomass conversion for biodiesel, the underlying complexity in integrating different processes with varying process conditions incurs costs. SCF process allows biodiesel production to be conducted without addition of catalyst.[158] By implementation of SCF method, catalytic *in situ* or reactive extraction process successfully combines the extraction and reaction phase together in a single processing unit. Production of biodiesel using non-catalytic SCF was first pioneered by Saka and Kusdiana[159] to study another alternative to conventional catalytic process which had slow reaction rates due to methanol/oil miscibility and polarity limitations. In addition, usage of homogeneous catalyst in biodiesel processing will add extra burden to the product purification after the reaction. Since majority of SCFs have low boiling points, they can be easily recovered from product mixtures and to be reused again with minimal purification. $ScCO_2$ is one of the most popular SCFs and has been regarded as one of the cleaner extraction agents for lipids and oils from solid seeds.[160] The polarity of CO_2 in oil extraction is greatly reduced and thus renders it to be miscible with non-polar lipids inside the solid seeds. Moreover, reactions perform at elevated temperature and pressure will usually have higher reaction rate and thus minimize the time required for optimum conversion.[159] Furthermore, numerous studies have been reported that SCF process will normally exhibit higher tolerance to impurity contents such as free fatty acids (FFA) and moisture.[161,162] This contradicts to conventional catalytic process where larger amount of impurities will promote side-reactions such as hydrolysis and saponification which reduced the biodiesel yield.[163]

Supercritical fluids gained an increasingly attention in many cleaning industries during the past decades due to their unique properties. The cleaning technology plays an important role in product quality during the remanufacturing process since remanufacturing cleaning often the main source of pollution. $ScCO_2$ cleaning has enormous potential in the remanufacturing cleaning application as CO_2 is plentiful, nonflammable, recyclable, nontoxic and inexpensive. In addition, $scCO_2$ is typically performed in closed-loop system which leads to be environmental friendly and reduced waste disposal costs. Liu *et al*.[164] investigated $scCO_2$ as a greener solution for remanufacturing cleaning process based on engine lubricating oil and grease. The effect of decontamination rate with variation of cleaning pressure, temperature and time by $scCO_2$ was studied. Experimental results showed that the $scCO_2$

Table I. Several Studies of PLA/Clay Blends Using Supercritical Fluid Method[a]

Blend(s)	Material Characteristic	Percentage of Material Loading	Method / Parameters of Blending	Result	Ref.
L-PLA; L-PLA/Clay	PLA=130,000 g mol^{-1} (molecular weight) Cloisite®20A=29 wt% (organic fraction); 2.4 nm (interlayer spacing) Cloisite®30B=20 wt% (organic fraction); 1.8 nm (interlayer spacing)	Clay=3, 10, 35, and 50 wt% (35 and 50 wt% were used as masterbatches.	*In situ* ring opening polymerization in $scCO_2$, then dilution of masterbatches into commercial L-PLA by melt blending.	Significant improvement of stiffness, toughness and impact resistance have been observed for the L-PLA/clay nanocomposites compared to pure matrix.	[155]
D-PLA D-PLA/Clay	Cloisite 93A=90%<13 μm, 50%<6 μm, 10%<2 μm (size distribution)	Clay=1 and 2.5 wt%	Pure polymer and polymer/clay nanocomposites were prepared using construct synthesis by $scCO_2$ method.	Porous resorbable D-PLA/clay exhibited a 2.5-fold increasein compressive and strength compared to pure polymer and greater biocompatibility than that of PS culture plate controls.	[156]
PLA/PHBV PLA/PHBV/ Clay	D-PLA=4% D-lactic acid monomer. PHBV=1.24 (specific gravity); 7 g/10 min (melt flow index); 158 °C (melting temperature); 1.25 g/cm^3 (density) Cloisite®30B=29 wt% (organic fraction); 1.84 nm (interlayer spacing)	PLA/PHBV blends with ratio 85/15 and 70/30 wt% and extra 4 wt% nanoclay for PLA/PHBV/ clay nanocomposites	The blends were compounded using a twin-screw extruder with temperature of barrel was in the range 165 to 180 °C. The screw speed was 100 rpm. Using scN_2 as physical blowing agent in the microcellular injection molding.	PLA/PHBV/clay nanocomposites showed a higher modulus and greater melt strength than PLA/PHBV blend. The addition of nanoclay also decreased the average cell size and increased the cell density of microcellular.	[157]
PLAPLA/Clay	PLA=linear with 4.5% D-lactide content	Clay=0-5 wt%	PLA and nanoclay (0.5, 1, and 2 wt%) with masterbatch (PLA/5 wt% clay) were dry-blended and melt-extruded using a counter-rotating twin-screw extruder at 180 °C with rotator speed at 150 rpm. Continous extrusion foaming using $scCO_2$	The X-ray diffraction and TEM images showed a high degree of exfoliation of nanoclay in PLA. The PLA crystallization kinetics was significantly enhanced. Both the cell density and expansion ratio were greatly promoted with increased clay content and the dissolved CO_2.	[145]

[a]PLA: Polylactic acid; PS: polystyrene; PHBV: polyhydroxybutyrate-valerate; TEM: transmission electron microscopy.

cleaning technique is an effective tool to remove some of the most common compounds of contaminants attached on the core surface, namely lubricating oil and grease, *etc*, compare to conventional method. By demonstrating the effects of pressure, temperature and time of cleaning effects, the optimum technological cleaning parameters were obtained. The $scCO_2$ cleaning has the low environment impact due to the fractional separation of the residue and the complete recovery of carbon dioxide. Cleansing agents play an essential part in many oil and grease removal applications and can be grouped into two categories; solvents and aqueous detergents. Several solvents have been used according to the required cleanliness such as chlorinated organic solvents, hydrocarbons, fluorocarbons and alcohols. Residence in Japan widely used chlorinated solvent which covered around 31% of the total shipment of cleansing agents in 2007, followed by aqueous detergents (27%), hydrocarbons (19%) and alcohols (16%).[165] Nowadays, the traditional cleaning solvents are still being used, albeit in more restricted and regulated manner. As an example, chlorinated organic solvents are able to remove oil and grease efficiently and economically. Unfortunately, they also have environment disadvantages as the facts that they release volatile organic compounds (VOCs) into the atmosphere, toxic impact on the environment and take long period of time for extraction with high cost of managing the degraded liquids and chlorinated product residues.[166,167] A number of alternative cleansing agents are possible approach as replacement such as aqueous solutions of detergents and emulsifiers. However, drawbacks to this approach include the production of large quantities of contaminated wash solution which, in most cases, must be handled as hazardous. As a consequence, the use of $scCO_2$ is an innovative replacement of traditional organic solvents, and the technique has been rapidly growing in parallel with the increased more stringent legislation rules against the use of VOCs.[168]

Another implementation of $scCO_2$ in industry is in food waste processing as the method use green solvent to meet the environment friendly requirement, in which renewable sources are used and the product do not offer environmental risks. Several researches have concentrated their efforts in the recovery and processing of compounds from fruits and vegetables wastes using extraction, fractionation/purification and encapsulation techniques. Wijngaard *et al*.[169] reported pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE) are gaining popularity due to their ability to increase target molecule specificity and reduce waste solvent production. However, SFE technique is appropriated to extract non polar substances, thus it does not present good performance to recovery compounds from wastes rich in water. The polarity of PLE is a good alternative, since with the use of solvents such as water and ethanol; the range of polar compounds and intermediate polarity can be covered. Furthermore, when the target compound is polar, PLE can be directly applied on wet samples. Table II shown recent published paper using supercritical and subcritical fluids to obtain compounds from fruits and vegetables.

Agriculture industries produce several wastes such as biomass and fermentation by-product from sugarcane processing; and shells from corn, wheat, rice, *etc*, which can be used for several reaction processes such as hydrolysis, gasification and biocatalysis. Lü *et al*.[181] used $scCO_2$ with water-ethanol as co-solvent to pre-treat corn stover and enhance its enzymatic hydrolysis. They obtained the highest sugar yield (77.8%) for the corn stover pretreated with CO_2/water-ethanol at 15 MPa and 180 °C for 1 h. After the pre-treatment, the percentage of cellulose increased 33% and the percentages of hemicellulose and lignin decreased 23% and 4%, respectively. Prado *et al*.[182] subcritical water process to direct hydrolysis of sugarcane bagasse to produce fermentable sugars. They observed the liquefaction degree of the sugarcane bagasse was not affected by water flow rat, and increased with temperature. The maximum liquefaction degree was of 95% for hydrolysis at 251 °C and 33 mL/min and at higher temperature, the hydrolysis process was faster, requiring 16 min.

Another source of pollutants is fish processing which generated wastes such as pieces of fish, scales and skin, viscera, *etc*. These wastes are usually destined to fish flour production for animal feed, or even thrown into rivers and seas, leading to environmental problems. Regarding to these issues, adding value to fish wastes has been the focus of many recent research works. A list of researches has indicated the nutritional impor-

Table II. Supercritical Technologies Applied to Food and Vegetables[170]

Process	Technique	Source	Target Compounds	Solvent	Parameters	Ref.
Extraction	SFE	Peach seeds	Phytosterols	CO_2	40 °C, 20 MPa	[171]
Extraction	SFE	Blackberry bagasse	Anthocyanins	CO_2, water	60 °C, 15 MPa	[172]
Extraction	SFE	By-product of the carob bean gum	Phenolic	CO_2, water, ethanol	40 °C, 22 MPa	[173]
Extraction	SFE	Pisco residues	Phenolics	CO_2, ethanol	40 °C, 20 MPa	[174]
Extraction	SFE	Tamarillo waste	Antioxidants	CO_2, ethanol	50 °C, 30 MPa	[175]
Extraction	SFE	Citrus peel	Volatile oils	CO_2	35 °C, 10 MPa	[176]
Extraction	PLE	Apple wastes	Flavonols	Water	120 °C, 10.3 MPa	[177]
Extraction	PLE	Potato peel	Anthocyanins	Ethanol, acidified water	80 °C, 10 MPa	[178]
Extraction	PLE	Jabuticaba skin	Anthocyanins	Ethanol	80 °C, 5 MPa	[179]
Extraction	PLE	Apple pomace	Phenolic, antioxidant	Water, ethanol	102 °C	[180]

tance of this type of researches. Mezzomo *et al*.,[183] Amiguet *et al*.[184] and Aguiar *et al*.[185] using $scCO_2$ technique to obtain compounds such as carotenoids from shrimp residue, polyunsaturated fatty acids from Northern shrimp and from striped weakfish, respectively. Mezzomo *et al*.[186] produced particles containing carotenoids from shrimp residue using Pluronic F127/modified starch as carrier material with processing parameters 35 °C and 10 MPa. The authors reached 93% efficiency with particles 0.8-0.7 μm.

Some studies have been found making references to supercritical method. Shin *et al*.[187] investigated supercritical methanol transesterification of refined pork lard, using 45:1 methanol to pork ratio, at 335 °C with 500 rpm agitation speed, at 20 MPa pressure over 15 min reaction duration and resulted in a maximum yield of 89.91% of fatty acid methyl esters. The author and co-workers concluded that supercritical methanol method under such conditions was equally applicable even for waste lard samples containing higher amounts of free fatty acid and water. Marulanda *et al*.[188] found the supercritical methanol transesterification of chicken fat that achieved up to 88% biodiesel yield at 400 °C, 41.1 MPa, methanol/fat molar ratio of 6:1 in 5 min of reaction. Reaction time for supercritical methanol transesterification is much lower as compared to those homogenous, heterogeneous and enzymatic catalytic routes of synthesis. For example, Bhatti *et al*.[189] obtained higher ester yields up-to 99% from chicken fat after 24 h by acid catalysis with sulphuric acid at temperature 50 °C and atmosphere pressure.

Outcomes of Review and Future Trends

This review covers mainly the development of supercritical fluid CO_2-assisted in clay dispersion and foaming processes over a decade. The commercial success of an SCF-polymer composite process lies not only in the process design, but also in understanding other aspects relevant to the process. Therefore, we give detailed attention to various aspects related to melt processing such as polymer/clay-CO_2 interaction, solubility and viscosity reduction. The discussion should help to provide a more complete picture of supercritical technology applicable to molten polymer in enhancing related properties. Moreover, CO_2 plays the role as a plasticizer in many polymers compounding where the viscosity of the matrix is reduced by dissolved CO_2 and consequently, conversion is increased by enhancing mass transfer. Particle size, shape and surface modification make a significant contribution on filler dispersion in polymer matrix.

Clearly, the solubility of a wide range of polymers in SCF can be controlled by employing additional physical and chemical factors, as well as modifying the operational methods. Thermal transition is one of the major aspects that should be considered. The consequences of various quench processes on the final product morphology and the relationship with the kinetics of the phase separation processes must be better revealed and described. Process dynamics must be related to polymer chain dynamics and the transitional phenomenon in polymers. The crystallization of polymers from SCF at high pressure often leads to not only different solid-fluid boundary conditions[45,135] but also to different crystalline morphologies with multiplicity, although this matter is not discussed in detail. We anticipate that new exploration in the future will include more information on the additional details of crystalline morphology.

The coupling of extrusion and $scCO_2$-assisted extrusion should be explored more because most thermoplastics are potential candidates on using this technique. Nucleation, growth and coalescence phenomena, coupled with factors such as expansion rate, average pore diameter and density, can control the structure of polymeric foams. However, this technology is still new, and further developments of both experimental and modelling studies are necessary for better understanding prior to industrial use.

Conclusions

In summary, this article provides an overview on the synthesis of polymer nanocomposites in $scCO_2$ *via* melt blending method. $scCO_2$ has demonstrated to be a viable alternative to conventional solvents. Apart from the properties of nanocomposites, the degree of dispersion of nanoparticles in polymers, as well as the interfacial interaction, play important roles in enhancing or limiting the overall properties of the system. A wide range of applications of $scCO_2$ clearly suggests a bright future of supercritical fluid in assisting polymer processing. As a simple and universal synthetic approach, the technique can be easily applied to synthesize wider polymer nanocomposites.

References

(1) P. Aranda and E. Ruiz-hitzky, *Chem. Mater.*, **4**, 1395 (1992).
(2) S. Horsch, G. Serhatkulu, E. Gulari, and R. M. Kannan, *Polymer*, **47**, 7485 (2006).
(3) S. S. H. Rizvi, S. J. Mulvaney, and A. S. Sokhey, *Trends Food Sci. Technol.*, **6**, 209 (1995).
(4) K. Yang and R. Ozisik, *J. Supercrit. Fluids*, **43**, 515 (2008).
(5) Y. Haldorai, J.-J. Shim, and K. T. Lim, *J. Supercrit. Fluids*, **71**, 45 (2012).
(6) S. P. Nalawade, F. Picchioni, and L. P. B. M. Janssen, *Prog. Polym. Sci.*, **31**, 19 (2006).
(7) O. Muth, T. Hirth, and H. Vogel, *J. Supercrit. Fluids*, **17**, 65 (2000).
(8) M. Rätzsch, H. Bucka, A. Hesse, and M. Arnold, *J. Macromol. Sci. Part A*, **33**, 913 (1996).
(9) F. Su and H. Huang, *J. Supercrit. Fluids*, **56**, 114 (2011).
(10) D.-C. Li, T. Liu, L. Zhao, and W.-K. Yuan, *J. Supercrit. Fluids*, **60**, 89 (2011).
(11) Z. Dong, Z. Liu, B. Han, X. Pei, L. Liu, and G. Yang, *J. Supercrit. Fluids*, **31**, 67 (2004).
(12) Z. Liu, L. Song, X. Dai, G. Yang, B. Han, and J. Xu, *Polymer*, **43**, 1183 (2002).

(13) Y.-M. Wang, Y.-J. Wang, and X.-B. Lu, *Polymer*, **49**, 474 (2008).
(14) G.-S. Tong, T. Liu, G.-H. Hu, L. Zhao, and W.-K. Yuan, *J. Supercrit. Fluids*, **43**, 64 (2007).
(15) Z. Liu, Z. Dong, B. Han, J. Wang, J. He, and G. Yang, *Chem. Mater.*, **14**, 4619 (2002).
(16) K. Cao, Z. Shen, Z. Yao, B. Qu, X. Pang, Z. Lu, Y. Li, and Z. Chen, *Chem. Eng. Sci.*, **65**, 1621 (2010).
(17) T. Liu, G.-H. Hu, G. Tong, L. Zhao, G. Cao, and W. Yuan, *Ind. Eng. Chem. Res.*, **44**, 4292 (2005).
(18) M. Soares da Silva, R. Viveiros, M. B. Coelho, A. Aguiar-Ricardo, and T. Casimiro, *Chem. Eng. Sci.*, **68**, 94 (2012).
(19) M. Drobek, J. Motuzas, V. Durand, M. Duchateau, C. Charmette, A. Hertz, C. Loubat, and A. Julbe, *J. Memb. Sci.*, **429**, 428 (2013).
(20) H. Adachi, K. Taki, S. Nagamine, A. Yusa, and M. Ohshima, *J. Supercrit. Fluids*, **49**, 265 (2009).
(21) C. A. García-González, A. Vega-González, A. M. López-Periago, P. Subra-Paternault, and C. Domingo, *Acta Biomater.*, **5**, 1094 (2009).
(22) M. R. Mauricio, F. C. G. Manso, M. H. Kunita, D. S. Velasco, A. C. Bento, E. C. Muniz, G. M. de Carvalho, and A. F. Rubira, *Compos. Part A Appl. Sci. Manuf.*, **42**, 757 (2011).
(23) P. Svoboda, K. Trivedi, D. Svobodova, K. Kolomaznik, and T. Inoue, *Polym. Test.*, **31**, 444 (2012).
(24) J. Chen, T. Liu, W. Yuan, and L. Zhao, *J. Supercrit. Fluids*, **77**, 33 (2013).
(25) K.-H. Kim, Z.-H. Shon, H. T. Nguyen, and E.-C. Jeon, *Atmos. Environ.*, **45**, 1369 (2011).
(26) C. Balsiger, C. Holliger, and P. Höhener, *Chemosphere*, **61**, 361 (2005).
(27) International Geophysics, Vol. 71, *Chemistry of the Natural Atmosphere*, Elsevier, New York, 2000, pp 264-345.
(28) J. S. Colton and N. P. Suh, *Polym. Eng. Sci.*, **27**, 500 (1987).
(29) W. Zhai, J. Yu, L. Wu, W. Ma, and J. He, *Polymer*, **47**, 7580 (2006).
(30) X.-L. Jiang, T. Liu, Z.-M. Xu, L. Zhao, G.-H. Hu, and W.-K. Yuan, *J. Supercrit. Fluids*, **48**, 167 (2009).
(31) D. F. Baldwin, C. B. Park, and N. P. Suh, *Polym. Eng. Sci.*, **36**, 1437 (1996).
(32) D. F. Baldwin, C. B. Park, and N. P. Suh, *Polym. Eng. Sci.*, **36**, 1446 (1996).
(33) S. T. Lee, L. Kareko, and J. Jun, *J. Cell. Plast.*, **44**, 293 (2008).
(34) S. Pilla, S. G. Kim, G. K. Auer, S. Gong, and C. B. Park, *Polym. Eng. Sci.*, **49**, 1653 (2009).
(35) Y. Di, S. Iannace, E. Di Maio, and L. Nicolais, *Macromol. Mater. Eng.*, **290**, 1083 (2005).
(36) D. Li, T. Liu, L. Zhao, X. Lian, and W. Yuan, *Ind. Eng. Chem. Res.*, **50**, 1997 (2011).
(37) T. Miyata and T. Masuko, *Polymer*, **39**, 5515 (1998).
(38) A. Wong, S. N. Leung, G. Y. G. Li, and C. B. Park, *Ind. Eng. Chem. Res.*, **46**, 7107 (2007).
(39) L.-Q. Xu and H.-X. Huang, *Ind. Eng. Chem. Res.*, **53**, 2277 (2014).
(40) J. Yang, L. Huang, Y. Zhang, F. Chen, P. Fan, M. Zhong, and S. Yeh, *Ind. Eng. Chem. Res.*, **52**, 14169 (2013).
(41) C. B. Park and N. P. Suh, *Polym. Eng. Sci.*, **36**, 34 (1996).
(42) A. Shariati and C. J. Peters, *Curr. Opin. Solid State Mater. Sci.*, **7**, 371 (2003).
(43) Y. Hakuta, H. Hayashi, and K. Arai, *Curr. Opin. Solid State Mater. Sci.*, **7**, 341 (2003).
(44) H. Okamoto and K. Danjo, *Adv. Drug Deliv. Rev.*, **60**, 433 (2008).
(45) N. Foster, R. Mammucari, F. Dehghani, A. Barrett, K. Bezanehtak, E. Coen, G. Combes, L. Meure, A. Ng, H. L. Regtop, and A. Tandya, *Ind. Eng. Chem. Res.*, **42**, 6476 (2003).
(46) S.-D. Yeo and E. Kiran, *J. Supercrit. Fluids*, **34**, 287 (2005).
(47) S. M. Pourmortazavi and S. S. Hajimirsadeghi, *Ind. Eng. Chem. Res.*, **44**, 6523 (2005).
(48) A. Martín and M. J. Cocero, *Adv. Drug Deliv. Rev.*, **60**, 339 (2008).
(49) I. Pasquali and R. Bettini, *Int. J. Pharm.*, **364**, 176 (2008).
(50) K. Byrappa, S. Ohara, and T. Adschiri, *Adv. Drug Deliv. Rev.*, **60**, 299 (2008).
(51) A. Tabernero, E. M. Martín del Valle, and M. A. Galán, *Chem. Eng. Process. Process Intensif.*, **60**, 9 (2012).
(52) I. Kikic, M. Lora, and A. Bertucco, *Ind. Eng. Chem. Res.*, **37**, 1577 (1998).
(53) A. Blasig, C. Shi, R. M. Enick, and M. C. Thies, *Ind. Eng. Chem. Res.*, **41**, 4976 (2002).
(54) Y. Chernyak, F. Henon, R. B. Harris, R. D. Gould, R. K. Franklin, J. R. Edwards, J. M. DeSimone, and R. G. Carbonell, *Ind. Eng. Chem. Res.*, **40**, 6118 (2001).
(55) B. Kongsombut, A. Tsutsumi, N. Suankaew, and T. Charinpanitkul, *Ind. Eng. Chem. Res.*, **48**, 11230 (2009).
(56) A. K. Lele and A. D. Shine, *Ind. Eng. Chem. Res.*, **33**, 1476 (1994).
(57) G.-T. Liu and K. Nagahama, *Ind. Eng. Chem. Res.*, **35**, 4626 (1996).
(58) M. J. Meziani, P. Pathak, W. Wang, T. Desai, A. Patil, and Y.-P. Sun, *Ind. Eng. Chem. Res.*, **44**, 4594 (2005).
(59) A. Montes, A. A. Litwinowicz, U. Gradl, M. D. Gordillo, C. Pereyra, and E. J. Martínez de la Ossa, *Ind. Eng. Chem. Res.*, **53**, 474 (2013).
(60) R. Salinas-Hernández, F. A. Ruiz-Treviño, C.-H. Ortiz-Estrada, G. Luna-Bárcenas, Y. Prokhorov, J. F. J. Alvarado, and I. C. Sanchez, *Ind. Eng. Chem. Res.*, **48**, 769 (2008).
(61) A. Sane and M. C. Thies, *J. Phys. Chem. B*, **109**, 19688. (2005).
(62) Y.-P. Sun, R. Guduru, F. Lin, and T. Whiteside, *Ind. Eng. Chem. Res.*, **39**, 4663 (2000).
(63) Y.-P. Sun, H. W. Rollins, and R. Guduru, *Chem. Mater.*, **11**, 7 (1998).
(64) R. Thakur and R. B. Gupta, *Ind. Eng. Chem. Res.*, **44**, 7380 (2005).
(65) Q. L. Suo, W. Z. He, Y. C. Huang, C. P. Li, H. L. Hong, Y. X. Li, and M. Da Zhu, *Powder Technol.*, **154**, 110 (2005).
(66) A.-Z. Chen, Y. Li, F.-T. Chau, T.-Y. Lau, J.-Y. Hu, Z. Zhao, and D. K. Mok, *J. Supercrit. Fluids*, **49**, 394 (2009).
(67) A.-Z. Chen, L. Li, S.-B. Wang, C. Zhao, Y.-G. Liu, G.-Y. Wang, and Z. Zhao, *J. Supercrit. Fluids*, **67**, 7 (2012).
(68) E. Franceschi, A. M. De Cesaro, S. R. S. Ferreira, and J. Vladimir Oliveira, *J. Food Eng.*, **95**, 656 (2009).
(69) D. L. Boschetto, I. Dalmolin, A. M. de Cesaro, A. A. Rigo, S. R. S. Ferreira, M. A. A. Meireles, E. A. C. Batista, and J. Vladimir Oliveira, *Ind. Crops Prod.*, **50**, 352 (2013).
(70) Y.-Z. Zhang, X.-M. Liao, G.-F. Yin, P. Yuan, Z.-B. Huang, J.-W. Gu, Y.-D. Yao, and X.-C. Chen, *Powder Technol.*, **221**, 343 (2012).
(71) H. Jin, S. Li, D. Hu, and Y. Zhao, *Powder Technol.*, **227**, 17 (2012).
(72) F. R. S. Machado Jr, D. F. Reis, D. L. Boschetto, J. F. M. Burkert,

S. R. S. Ferreira, J. V. Oliveira, and C. A. V. Burkert, *Ind. Crops Prod.*, **54**, 17 (2014).
(73) Y. Kang, G. Yin, P. Ouyang, Z. Huang, Y. Yao, X. Liao, A. Chen, and X. Pu, *J. Colloid Interface Sci.*, **322**, 87 (2008).
(74) D. Hu, C. Lin, L. Liu, S. Li, and Y. Zhao, *J. Food Eng.*, **109**, 545 (2012).
(75) E. Franceschi, A. M. De Cesaro, M. Feiten, S. R. S. Ferreira, C. Dariva, M. H. Kunita, A. F. Rubira, E. C. Muniz, M. L. Corazza, and J. V. Oliveira, *J. Supercrit. Fluids*, **47**, 259 (2008).
(76) A. Tabernero, E. M. Martín del Valle, and M. A. Galán, *Powder Technol.*, **217**, 177 (2012).
(77) G. H. Chong, R. Yunus, T. S. Y. Choong, N. Abdullah, and S. Y. Spotar, *J. Supercrit. Fluids*, **60**, 69 (2011).
(78) N. Ventosa, S. Sala, and J. Veciana, *J. Supercrit. Fluids*, **26**, 33 (2003).
(79) E. N. Lay, *J. Chem. Eng. Data*, **55**, 223 (2009).
(80) M. Rossmann, A. Braeuer, S. Dowy, T. G. Gallinger, A. Leipertz, and E. Schluecker, *J. Supercrit. Fluids*, **66**, 350 (2012).
(81) K. Chen, X. Zhang, J. Pan, W. Zhang, and W. Yin, *Powder Technol.*, **152**, 127 (2005).
(82) M.-W. Park and S.-D. Yeo, *Chem. Eng. Res. Des.*, **90**, 2202 (2012).
(83) S. A. B. V. de Melo, L. T. Danh, R. Mammucari, and N. R. Foster, *J. Supercrit. Fluids*, **93**, 112 (2014).
(84) B. Yu. Shekunov, J. Baldyga, and P. York, *Chem. Eng. Sci.*, **56**, 2421 (2001).
(85) S.-J. Park and S.-D. Yeo, *J. Supercrit. Fluids*, **47**, 85 (2008).
(86) E. Reverchon, *J. Supercrit. Fluids*, **15**, 1 (1999).
(87) S.-C. Chang, M.-J. Lee, and H.-M. Lin, *J. Supercrit. Fluids*, **40**, 420 (2007).
(88) V. J. Pereira, R. L. Matos, S. G. Cardoso, R. O. Soares, G. L. Santana, G. M. N. Costa, and S. A. B. Vieira de Melo, *J. Supercrit. Fluids*, **81**, 128 (2013).
(89) Y. Bakhbakhi, S. Alfadul, and A. Ajbar, *Eur. J. Pharm. Sci.*, **48**, 30 (2013).
(90) E. Elizondo, A. Córdoba, S. Sala, N. Ventosa, and J. Veciana, *J. Supercrit. Fluids*, **53**, 108 (2010).
(91) D. J. Jarmer, C. S. Lengsfeld, and T. W. Randolph, *J. Supercrit. Fluids*, **27**, 317 (2003).
(92) I.-H. Lin, P.-F. Liang, and C.-S. Tan, *J. Supercrit. Fluids*, **51**, 384 (2010).
(93) K. Wu and J. Li, *J. Supercrit. Fluids*, **46**, 211. (2008).
(94) S. Mawson, S. Kanakia, and K. P. Johnston, *Polymer*, **38**, 2957 (1997).
(95) S. Kunastitchai, L. Pichert, N. Sarisuta, and B. W. Müller, *Int. J. Pharm.*, **316**, 93 (2006).
(96) K. Moribe, M. Fukino, Y. Tozuka, K. Higashi, and K. Yamamoto, *Int. J. Pharm.*, **380**, 201 (2009).
(97) H.-H. Jeong, K.-P. Yoo, and J. S. Lim, *J. Ind. Eng. Chem.*, **14**, 77 (2008).
(98) W. Yu, F. Xia, H. Jin, C. Lin, Y. Zhao, S. Jiang, and L. He, *Chinese J. Chem. Eng.*, **16**, 956 (2008).
(99) H. Steckel, L. Pichert, and B. W. Müller, *Eur. J. Pharm. Biopharm.*, **57**, 507 (2004).
(100) J. Bleich, B. W. Müller, and W. Waßmus, *Int. J. Pharm.*, **97**, 111 (1993).
(101) J. Bleich, P. Kleinebudde, and B. W. Müller, *Int. J. Pharm.*, **106**, 77 (1994).
(102) A. Engwicht, U. Girreser, and B. W. Müller, *Int. J. Pharm.*, **185**, 61 (1999).
(103) M. Fraile, Ÿ. Martín, D. Deodato, S. Rodriguez-Rojo, I. D. Nogueira, A. L. Simplício, M. J. Cocero, and C. M. M. Duarte, *J. Supercrit. Fluids*, **81**, 226 (2013).
(104) J.-H. Yun, S.-M. Lee, J.-N. Park, and B.-S. Chun, *APCBEE Procedia*, **2**, 22 (2012).
(105) M. Brion, S. Jaspart, L. Perrone, G. Piel, and B. Evrard, *J. Supercrit. Fluids*, **51**, 50 (2009).
(106) J.-H. Yun, H.-Y. Lee, A. K. M. Asaduzzaman, and B.-S. Chun, *J. Ind. Eng. Chem.*, **19**, 686 (2013).
(107) E. de Paz, Á. Martín, and M. J. Cocero, *J. Supercrit. Fluids*, **72**, 125 (2012).
(108) E. J. Park, A. P. Richez, N. A. Birkin, H. Lee, N. Arrowsmith, K. J. Thurecht, and S. M. Howdle, *Polymer*, **52**, 5403 (2011).
(109) Y.-M. Wang, Y. Pan, Y.-L. Wang, G.-P. Wu, Y.-J. Wang, L. N. Nikitin, and X.-B. Lu, *J. Supercrit. Fluids*, **44**, 62 (2008).
(110) K. S. Oh, W. Bae, and H. Kim, *Eur. Polym. J.*, **44**, 415 (2008).
(111) P. O'Connor, R. Yang, W. M. Carroll, Y. Rochev, and F. Aldabbagh, *Eur. Polym. J.*, **48**, 1279 (2012).
(112) H. S. Hwang, W.-K. Lee, S.-S. Hong, S.-H. Jin, and K. T. Lim, *J. Supercrit. Fluids*, **39**, 409 (2007).
(113) H. S. Ganapathy, H. S. Hwang, Y. T. Jeong, W.-K. Lee, and K. T. Lim, *Eur. Polym. J.*, **43**, 119 (2007).
(114) Z. Wang, Y. J. Yang, Q. Dong, T. Liu, and C. P. Hu, *Polymer*, **47**, 7670 (2006).
(115) H. Yuvaraj, H. S. Hwang, W. S. Kim, H. G. Kim, E. D. Jeong, and K. T. Lim, *Eur. Polym. J.*, **44**, 2253 (2008).
(116) C. W. Manke, E. Gulari, D. F. Mielewski, and E. C. Lee, US Patent 6,469,073 BI (2002).
(117) D. F. Mielewski, E. C. Lee, C. W. Manke, and W. Gulari, US Patent 6,753,360 B2 (2004).
(118) M. Garcia-Leiner and A. J. Lesser, *ANTEC Conference Proceedings*, Society of Plastics Engineers, Nashville, **2**, 1528 (2003).
(119) D. L. Tomasko, X. Han, D. Liu, and W. Gao, *Curr. Opin. Solid State Mater. Sci.*, **7**, 407 (2003).
(120) S. S. Ray and M. Okamoto, *Prog. Mater. Sci.*, **28**, 1539 (2003).
(121) S. S. Ray, K. Okamoto, and M. Okamoto, *Macromolecules*, **36**, 2355 (2003).
(122) J. Ma, E. Bilotti, T. Peijs, and J. A. Darr, *Eur. Polym. J.*, **43**, 4931 (2007).
(123) E. Bilotti, H. R. Fischer, and T. Peijs, *J. Appl. Polym. Sci.*, **107**, 1116 (2008).
(124) L. Urbanczyk, C. Calberg, F. Stassin, M. Alexandre, R. Jérôme, C. Jérôme, and C. Detrembleur, *Polymer*, **49**, 3979 (2008).
(125) M. Devalckenaere, R. Je, C. Henrist, and P. Dubois, *Polymer*, **44**, 2033 (2003).
(126) C. Broekaert, S. Peeterbroeck, S. Benali, F. Monteverde, L. Bonnaud, M. Alexandre, and P. Dubois, *Eur. Polym. J.*, **43**, 4160 (2007).
(127) L. Urbanczyk, F. Ngoundjo, M. Alexandre, C. Jérôme, C. Detrembleur, and C. Calberg, *Eur. Polym. J.*, **45**, 643 (2009).
(128) S. Doroudiani, C. B. Park, and M. T. Kortschot, *Polym. Eng. Sci.*, **36**, 2645 (1996).
(129) T. T. Van Ngo, J. Duchet-Rumeau, A. K. Whittaker, and J.-F. Gerard, *Polymer*, **51**, 3436 (2010).
(130) S. Horsch, G. Serhatkulu, E. Gulari, and R. M. Kannan, *Polymer*, **47**, 7485 (2006).
(131) A. Tsimpliaraki, I. Tsivintzelis, S. I. Marras, I. Zuburtikudis, and C. Panayiotou, *J. Supercrit. Fluids*, **57**, 278 (2011).

(132) N. Le Moigne, M. Sauceau, M. Benyakhlef, R. Jemai, J.-C. Benezet, E. Rodier, J.-M. Lopez-Cuesta, and J. Fages, *Eur. Polym. J.*, **61**, 157 (2014).
(133) S. Lee, D. Shim, and J. Lee, *Macromol. Res.*, **16**, 6 (2008).
(134) W. Zhai, T. Kuboki, L. Wang, C. B. Park, E. K. Lee, and H. E. Naguib, *Ind. Eng. Chem. Res.*, **49**, 9834 (2010).
(135) M. Nofar, K. Majithiya, T. Kuboki, and C. B. Park, *J. Cell. Plast.*, **48**, 271 (2012).
(136) M. A. Treece and J. P. Oberhauser, *J. Appl. Polym. Sci.*, **103**, 884 (2007).
(137) X. Han, C. Zeng, L. J. Lee, K. W. Koelling, and D. L. Tomasko, *Polym. Eng. Sci.*, **43**, 1261 (2003).
(138) Q. T. Nguyen and D. G. Baird, *Polymer*, **48**, 6923 (2007).
(139) C. Chen, J. Samaniuk, D. G. Baird, G. Devoux, M. Zhang, R. B. Moore, and J. P. Quigley, *Polymer*, **53**, 1373 (2012).
(140) K. Goren, O. B. Okan, L. Chen, L. S. Schadler, and R. Ozisik, *J. Supercrit. Fluids*, **67**, 108 (2012).
(141) A. Tsimpliaraki, I. Tsivintzelis, S. I. Marras, I. Zuburtikudis, and C. Panayiotou, *J. Supercrit. Fluids*, **81**, 86 (2013).
(142) I. Tsivintzelis, E. Pavlidou, and C. Panayiotou, *J. Supercrit. Fluids*, **42**, 265 (2007).
(143) S. K. Goel and E. J. Beckman, *Polym. Eng. Sci.*, **34**, 1137 (1994).
(144) E. Kiran, *J. Supercrit. Fluids*, **54**, 308 (2010).
(145) W. Liu, X. Wang, H. Li, Z. Du, and C. Zhang, *J. Cell. Plast.*, **49**, 535 (2013).
(146) M. Keshtkar, M. Nofar, C. B. Park, and P. J. Carreau, *Polymer*, **55**, 4077 (2014).
(147) Y. Fujimoto, S. S. Ray, M. Okamoto, A. Ogami, K. Yamada, and K. Ueda, *Macromol. Rapid Commun.*, **24**, 457 (2003).
(148) S. Gogolewski, M. Jovanovic, S. M. Perren, J. G. Dillon, and M. K. Hughes, *Polym. Degrad. Stab.*, **40**, 13 (1993).
(149) D. H. S. Ramkumar and M. Bhattacharya, *Polym. Eng. Sci.*, **38**, 1426 (1998).
(150) L. Cabedo, D. Plackett, E. Giménez, and J. M. Lagarón, *J. Appl. Polym. Sci.*, **112**, 3669 (2009).
(151) P. Bordes, E. Hablot, E. Pollet, and L. Avérous, *Polym. Degrad. Stab.*, **94**, 789 (2009).
(152) H. Zhao, Z. Cui, X. Sun, L.-S. Turng, and X. Peng, *Ind. Eng. Chem. Res.*, **52**, 2569 (2013).
(153) H. Zhao, Z. Cui, X. Wang, L.-S. Turng, and X. Peng, *Compos. Part B Eng.*, **51**, 79 (2013).
(154) A. Javadi, Y. Srithep, C. C. Clemons, L.-S. Turng, and S. Gong, *J. Mater. Res.*, **27**, 1506 (2012).
(155) L. Urbanczyk, F. Ngoundjo, M. Alexandre, C. Jérôme, C. Detrembleur, and C. Calberg, *Eur. Polym. J.*, **45**, 643 (2009).
(156) K. C. Baker, M. Manitiu, R. Bellair, C. A. Gratopp, H. N. Herkowitz, and R. M. Kannan, *Acta Biomater.*, **7**, 3382 (2011).
(157) H. Zhao, Z. Cui, X. Wang, L.-S. Turng, and X. Peng, *Compos. Part B Eng.*, **51**, 79 (2013).
(158) K. T. Lee, S. Lim, Y. L. Pang, H. C. Ong, and W. T. Chong, *Prog. Energy Combust. Sci.*, **45**, 54 (2014).
(159) S. Saka and D. Kusdiana, *Fuel*, **80**, 225 (2001).
(160) E. Stahl, E. Schuetz, and H. K. Mangold, *J. Agric. Food Chem.*, **28**, 1153 (1980).
(161) N. M. Niza, K. T. Tan, K. T. Lee, and Z. Ahmad, *J. Supercrit. Fluids*, **79**, 73 (2013).
(162) D. Kusdiana and S. Saka, *Bioresour. Technol.*, **91**, 289 (2004).
(163) S. Suwito, G. Dragone, H. Sulistyo, B. Murachman, S. Purwono, and J. Teixeira, *Front. Chem. Sci. Eng.*, **6**, 210 (2012).
(164) W. Liu, B. Zhang, Y. Li, Y. He, and H. Zhang, *Appl. Surf. Sci.*, **292**, 142 (2014).
(165) E. Kikuchi, Y. Kikuchi, and M. Hirao, *J. Clean. Prod.*, **19**, 414 (2011).
(166) M. G. Bernardo-Gil, I. M. G. Lopes, M. Casquilho, M. A. Ribeiro, M. M. Esquível, and J. Empis, *J. Supercrit. Fluids*, **40**, 344 (2007).
(167) G. Vasapollo, L. Longo, L. Rescio, and L. Ciurlia, *J. Supercrit. Fluids*, **29**, 87 (2004).
(168) H. Rajaei, A. Amin, A. Golchehre, and F. Esmaeilzadeh, *J. Supercrit. Fluids*, **67**, 1 (2012).
(169) H. Wijngaard, M. B. Hossain, D. K. Rai, and N. Brunton, *Food Res. Int.*, **46**, 505 (2012).
(170) J. Viganó, A. P. D. F. Machado, and J. Martínez, *J. Supercrit. Fluids*, **96**, 272 (2014).
(171) M. S. Ekinci and M. Gürü, *J. Supercrit. Fluids*, **92**, 319 (2014).
(172) J. L. Pasquel Reátegui, A. P. da F. Machado, G. F. Barbero, C. A. Rezende, and J. Martínez, *J. Supercrit. Fluids*, **94**, 223 (2014).
(173) L. B. Roseiro, L. C. Duarte, D. L. Oliveira, R. Roque, M. G. Bernardo-Gil, A. I. Martins, C. Sepúlveda, J. Almeida, M. Meireles, F. M. Gírio, and A. P. Rauter, *Ind. Crops Prod.*, **47**, 132 (2013).
(174) A. M. Farías-Campomanes, M. A. Rostagno, and M. A. A. Meireles, *J. Supercrit. Fluids*, **77**, 70 (2013).
(175) H. I. Castro-Vargas, P. Benelli, S. R. S. Ferreira, and F. Parada-Alfonso, *J. Supercrit. Fluids*, **76**, 17 (2013).
(176) J. Omar, I. Alonso, A. Garaikoetxea, and N. Etxebarria, *Food Anal. Methods*, **6**, 1244 (2013).
(177) M. Plaza, V. Abrahamsson, and C. Turner, *J. Agric. Food Chem.*, **61**, 5500 (2013).
(178) L. C. Cardoso, C. M. Serrano, E. T. Quintero, C. P. López, R. M. Antezana, and E. J. de la Ossa, *Molecules*, **18**, 3137 (2013).
(179) D. T. Santos, P. C. Veggi, and M. A. A. Meireles *J. Food Eng.*, **108**, 444 (2012).
(180) H. Wijngaard and N. Brunton, *J. Agric. Food Chem.*, **57**, 10625 (2009).
(181) H. Lü, M. Ren, M. Zhang, and Y. Chen, *Chinese J. Chem. Eng.*, **21**, 551 (2013).
(182) J. M. Prado, L. A. Follegatti-Romero, T. Forster-Carneiro, M. A. Rostagno, F. Maugeri Filho, and M. A. A. Meireles, *J. Supercrit. Fluids*, **86**, 15 (2014).
(183) N. Mezzomo, J. Martínez, M. Maraschin, and S. R. S. Ferreira, *J. Supercrit. Fluids*, **74**, 22 (2013).
(184) V. Treyvaud Amiguet, K. L. Kramp, J. Mao, C. McRae, A. Goulah, L. E. Kimpe, J. M. Blais, and J. T. Arnason, *Food Chem.*, **130**, 853 (2012).
(185) A. C. Aguiar, J. V Visentainer, and J. Martínez, *J. Supercrit. Fluids*, **71**, 1 (2012).
(186) N. Mezzomo, E. de Paz, M. Maraschin, Á. Martín, M. J. Cocero, and S. R. S. Ferreira, *J. Supercrit. Fluids*, **66**, 342 (2012).
(187) H.-Y. Shin, S.-H. Lee, J.-H. Ryu, and S.-Y. Bae, *J. Supercrit. Fluids*, **61**, 134 (2012).
(188) V. F. Marulanda, G. Anitescu, and L. L. Tavlarides, *J. Supercrit. Fluids*, **54**, 53 (2010).
(189) H. N. Bhatti, M. A. Hanif, M. Qasim, and Ata-ur-Rehman, *Fuel*, **87**, 2961 (2008).